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Rice Straw Amendment and Sulfate Affecting Methane Production and Chemical Properties in Paddy Soils

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Abstract

Rice straw is an important organic source for paddy soil improvement, but it is also a source for methane (CH₄) fermentation in flooded paddy. In contrast, sulfate (SO₄²⁻) is a source of electron acceptor in anoxic condition which plays a role in reducing CH₄ production. Therefore, this incubation was conducted with the aim of investigating the effect of rice straw amendment in combination with SO₄²⁻ on some soil chemical change in 3 different-textured paddy soils. Five rice straw amendment rates, 0, 6.25, 12.50, 18.75 and 25 t/ha; and 2 rates of SO₄²⁻, 100 and 200 kg/ha were anaerobically incubated in loam, clay and loamy sand soils, arranged in 5×2 factorials with triplicate. Results showed that rice straw amendment significantly increased ($p \leq 0.01$) CH₄ production with increasing rate of rice straw positively correlated with labile organic carbon (LOC), pH, and electrical conductivity (EC) in all soil types, except for pH in loamy soil which was negatively correlated. However, 200 kg/ha of SO₄²⁻ had stronger potential to suppress CH₄ production than 100 kg/ha, which showed in clay and loamy sand. The highest range of CH₄ production was in clay followed by loam and loamy sand at all rates of rice straw, except at 25 t/ha of rice straw in loam and clay which gave the same range. In addition, LOC, pH and EC also significantly increased ($p \leq 0.001$) with increasing rate of rice straw regardless of SO₄²⁻ in each of soil types. The highest LOC and EC were found in clay followed by loam and loamy sand, but the same range of pH was observed in both of loam and clay, and lower in loamy sand. Although, rice straw application had potential to increase CH₄ production from paddy soils, it promoted soluble ions in soil.

Keywords: organic material, soil fertility, greenhouse gas, incubation experiment

1. Introduction

Rice paddy is one of the main emitters of anthropogenic greenhouse gases (GHG), which contribute to global warming. Recently, biotic carbon (C) sequestration was considered feasible for mitigating C emissions in the form of CO₂ and CH₄ to the atmosphere (1, 2). Previous study had reported that application of inorganic fertilizers resulted in significant increase in soil organic carbon (SOC) due to its positive effects on crop growth and in turn of crop C return to the soils; hence the integrated use of organic and inorganic fertilizers is necessary for soil productivity (3). CH₄ production and emission from soil were derived from C mineralization, and widely documented subject to soil temperature, moisture, pH, Eh and plant cultivars (4). In addition, labile soil organic fractions are very vulnerable to disturb and play a crucial role for C cycling and nutrient release. It has been also playing a major role for source and sink of GHG change such as CO₂ and CH₄ (5). Rice straw application in paddy soil showed a significant increase in CH₄ emissions (6). Whereas, SO₄²⁻ is a very important electron acceptor in anaerobic soil for SO₄²⁻ reduction process which plays a vital role in reducing CH₄ formation in wetland (7). Therefore, this soil incubation experiment was established in a laboratory in order to investigate CH₄ formation, LOC change, pH and EC characteristics from application of different rates of rice straw combined with SO₄²⁻ in anoxic condition within loamy, clayey and sandy loam paddy soils. The main hypothesis is that rice straw amendment in soils will enhance CH₄ formation, but SO₄²⁻ will slow down methanogenesis.

2. Materials and methods

2.1 Treatments, soil and incubation

The experiment was laid out in 5x2 factorials with triplicate, incorporated with 0, 6.25, 12.50, 18.75 and 25 t/ha of rice straw (RS) and 2 rates of SO₄²⁻ (100 and 200 kg/ha). SO₄²⁻ rates were derived from ammonium phosphate sulfate, [(NH₄)₂(H₂PO₄)(HSO₄)] (N-P₂O₅-K₂O: 16-20-0, 42 g SO₄²⁻/100 g). The loamy, clayey and sandy loam paddy soils were sampled from 0-15 cm depth in paddy fields in northeast of Thailand. The chemical and physical properties are shown in Table 1. The soil was air dried, and ground and passed through a 2 mm sieve. Enough amount of soil sample was pre-submerged in water for one week. Prior to the soil incubation, moisture content of the muddy soil was determined. A weight of muddy soil used in this incubation trial equivalent to 5 g of dried soil, was placed in a 60 ml serum bottle. Then, 0, 0.016, 0.032, 0.048 and 0.064 g of RS equivalent to 0, 6.25, 12.50, 18.75 and 25 t RS/ha, and 0.61 or 1.22 mg SO₄²⁻ equivalent to 100 or 200 kg SO₄²⁻/ha, respectively, were added in each bottle. The soil medium was shaken with a vortex shaker to expel any gas bubbles in soil slurry, and flushed the head space in the bottles by ejecting N₂ (99.99%) gas with 1.5 bar pressure. The bottle was closed immediately with butyl rubber stoppers and aluminum crimp top seals. They were wrapped up with aluminum foil to protect them from light radiation. The bottles were kept in laboratory ambience.

2.2 Gas samplings and soil analysis

Gas samplings were performed every week for 4 weeks. Before the actual gas samplings, the incubation samples were flushed with N₂ (99.99%) for 1 minute with

Table 1 Soils and rice straw (RS) properties used in the incubation experiment

Soils/ RS	Sand (%)	Silt (%)	Clay (%)	SO ₄ ²⁻ (mg/kg)	OC (%)	LOC (mg/kg)	TN (%)	C:N ratio
Loam	50.00	36.70	13.30	39.93	0.79	504	0.07	11.29
Clay	2.53	17.31	80.26	23.25	1.75	1730	0.16	10.94
Loamy sand	84.14	11.95	3.91	6.91	0.12	108	0.02	6.00
Rice straw	-	-	-	-	21.80	6670	0.60	36.33

1.5 bar pressure, sealed tight as mentioned previously and incubated again for 24 hours. Prior gas sampling the incubated samples were shaken for 1 minute to expel CH_4 in soil aggregates into the headspace, and 1 ml gas sample was taken from the headspace of incubation bottle by using an air-tight syringe. The concentration of CH_4 in the gas samples was analyzed using gas chromatograph (Shimadzu GC2014), detector temperature 200°C (FID), injection port 150°C , oven 180°C , stainless steel column 2 m length packed with unibead C. Carrier gas is He and retention time is 2.25 minutes. To calculate the CH_4 production the equation by Setyanto et al. (8) was used. Labile organic carbon (LOC) was analyzed by 33 mM permanganate-oxidation (KMnO_4) method (9). The pH and EC of flooded water were measured fitting to CH_4 and labile carbon analysis by using pH and EC meters, respectively. SO_4^{2-} content in soil was extracted with KH_2PO_4 and analyzed using turbidimetric method.

2.3 Statistical analysis

The data collected was analyzed statistically using Analysis of Variance (ANOVA) technique and treatment means were compared by using Duncan's Multiple Range Test (DMRT) with SAS statistical program.

3. Results and discussions

3.1 CH_4 production

Cumulative CH_4 productions (Fig. 1) significantly increased ($p \leq 0.01$) with increasing rate of rice straw in all the soil types. The maximum CH_4 productions at 25 t/ha of RS were 665.72, 555.81, and 265.81 $\text{mg CH}_4\text{-C kg}^{-1}$ in loam, clay and loamy sand, respectively. The highest range of CH_4 production was in clay at 6.25 to 18.75 t/ha levels of RS followed by loam and loamy sand of the same RS rates, except for 25 t/ha. RS amended soils in loam and clay were the same range. It was found that SO_4^{2-} had some potential to suppress CH_4 productions in clay and loamy sand because sulfate reducing microorganisms competed with methanogens in using carbon substrates (7). Simultaneously, SO_4^{2-} reduction was almost completed at the end of incubation (Fig. 2). CH_4 productions were significantly and positively correlated with LOC, pH and EC in all soil types, but significant negatively correlated with pH in loam during the first 2 weeks of incubation (Table 2). The mechanism concerning negative correlation between pH and CH_4 production in loam soil are not yet fully understood. The increase in EC coincided with an increase in CH_4 production could be attributed that they were dependable upon organic material decomposition

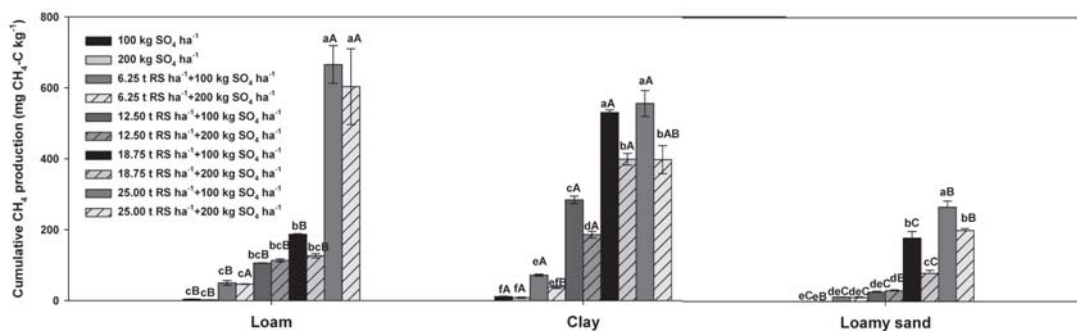


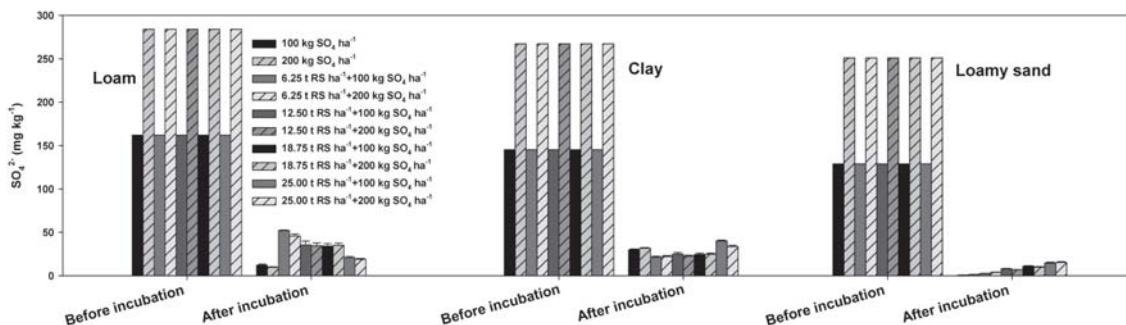
Fig. 1 Cumulative CH_4 productions in anoxic incubated soils affected by different rates of rice straw (RS) and SO_4^{2-} application, different letters showed significantly different at $p \leq 0.01$, vertical bars represent SE-mean. The lower case letters compare between the treatments within each soil type and the upper case letters compare the treatments between the three soil types

Table 2 Pearson correlation coefficient (r) between cumulative CH_4 and LOC, pH and EC within different rates of rice straw and SO_4^{2-} in different soil types after 4 weeks of anoxic incubation, n=30

Soil parameters	DOI	Loam (r)	Clay (r)	Loamy sand (r)
LOC (mg-C kg^{-1})	0	- 0.31	+ 0.76***	+ 0.79***
	7	+ 0.77***	+ 0.76 ***	+ 0.95***
	14	+ 0.37*	+ 0.68***	+ 0.88***
	21	- 0.09	+ 0.76***	+ 0.78***
	28	+ 0.90***	+ 0.81 ***	+ 0.80***
pH	0	- 0.07	+ 0.03	+ 0.76***
	7	- 0.62 ***	+ 0.68***	+ 0.48**
	14	- 0.86***	+ 0.31	+ 0.65***
	21	+ 0.07	+ 0.26	+ 0.67***
	28	+ 0.39*	+ 0.49 **	+ 0.75**
EC (dS m^{-1})	0	+ 0.42*	+ 0.61***	+ 0.31
	7	+ 0.86***	+ 0.79***	+ 0.91***
	14	+ 0.77***	+ 0.88***	+ 0.86***
	21	+ 0.77**	+ 0.71***	+ 0.90***
	28	+ 0.93***	+ 0.63***	+ 0.85***

*, ** and *** represented significant difference at ≤ 0.05 , 0.01 and 0.001, respectively

Note: r (+, -) = 1.0 to 0.7, 0.6 to 0.5, and >0.4 identified strong, moderate and weak association, respectively

**Fig.2** SO_4^{2-} reductions in 3 soil types at 4 weeks of anoxic incubation

by highly microbial activities. Several research findings related to our recent study have been reported. Lu et al. (10) reported that crop residue incorporation promotes CH_4 emission by addition of carbon substrate to the soil. Likewise, Bhattacharyya et al. (3) explained that rice straw decomposition produced acetate which is a key component for methanogen growth, and produced higher CH_4 as the increase of rice straw. In addition, Yaun et al. (11) explained that the stimulation of CH_4 production by rice straw application is because it served as relatively labile organic substrate which readily degraded to CH_4 . This is

in agreement with our results which showed that CH_4 production was positively correlated with LOC. Moreover, Gupta et al. (12) reported that LOC and pH are some of the factors that influence CH_4 production. Furthermore, another similarity to our results is the Yagi and Minami (13) findings which indicated that CH_4 emissions differed markedly with soil types. In general, considering among the three textural soils the ranges of LOC content and the ranges of CH_4 production were increasing in the same order as clay > loam > loamy sand. This could explain that soil textures determined LOC and CH_4 production in

incubated soil condition (2). Rice straw provided substrates for both SO_4^{2-} reducing microorganisms and methanogens. SO_4^{2-} reducing microorganisms may not conquer the capacity of methanogens in loamy soil, due to the imbalance between electron donors (rice straw) and electron acceptors (SO_4^{2-}). The number of moles of SO_4^{2-} in these studied soils may not enough to compete acetate with methanogens, hence not significant reduction of CH_4 production (7) in loamy soil. In this study, we found that the higher rate (200 kg/ha) of SO_4^{2-} had stronger potential to suppress CH_4 production than lower rate (100 kg/ha) as seen in clay and loamy sand soils amended with rice straw

3.2 Labile organic carbon (LOC)

According to the LOC contents in original soils (Table 1) 504, 1730, and 108 mg/kg, and the ranges at 4 weeks of incubation (Fig. 3a) 654 to 904, 1742 to 2201, and 130 to 351 mg/kg in loamy, clayey and loamy sand soils, respectively, it seems that the ranges of LOC though after incubated with RS showed the same trends of results as those of corresponding controls. These results indicated that soil texture was a factor determining the LOC storages in soils. Increasing the rate of rice straw amendment significantly increased ($p < 0.001$) soil LOC regardless of SO_4^{2-} combination in all soil types (Fig. 3a). The highest LOC was 2201.21 mg-C/kg in clayey soil with 25 t RS/ha followed by loam and loamy sand of the same treatment. Yuan et al. (11) reported that rice straw application stimulated LOC, and Majumder et al. (14) also found that the combination of N-P-K fertilizer and paddy straw application significantly increased total organic C including labile fractions. Moreover, Puttaso et al. (2) found that microaggregates stored the highest C content and stressed that microaggregates were the most important C storage location in the soil matrix. Their findings support our results that clay, which generally contains more microaggregates stored higher amounts of LOC than loam and loamy sand that contain more macro-aggregates.

3.3 Soil pH of flooded water

Rice straw amendment (Fig. 3b) significantly increased ($p \leq 0.001$) pH regardless of SO_4^{2-} in all soil types. Without considering to the treatments, the maximum pH in each soil was 7.04, 7.13 and 6.38 in loam, clay and loamy sand, respectively. Past experiments by Dong et al. (15) showed that rice straw application significantly increased pH of flooded soil. Ebid et al. (16) also proved that rice residues application markedly increased soil pH were commonly found in flooded acid soils due to the removal of protons from the soil system when Fe^{3+} , Mn^{4+} and SO_4^{2-} were reduced during anaerobic microbial respiration. This process might happen similarly to any type of easily decomposable organic materials as rice straw in soil solutions. Rukshana et al. (17) stated that C compound in plant material and initial soil pH regulated the direction and magnitude of soil pH change. Furthermore, Hairani and Susilawati (18) found that rice straw application caused differences in response patterns of soil pH change because of the differences in reduction ability of soil types.

3.4 Soil electrical conductivity of flooded water (EC)

As in LOC and pH, Electrical conductivities were significantly increased ($p \leq 0.001$) with the increasing rate of rice straw amendment regardless of SO_4^{2-} application in all soil types (Fig. 3c). Clay with RS of 25 t/ha gave the highest EC, 0.66 dS/m, followed by loam, 0.63 dS/m. In the context of soil EC, Ebid et al. (16) reported that rice residue application significantly enhanced soil EC. Moreover, Najafi (19) found that the EC of paddy soil solution was different in pattern depending on soil types, while Islam et al. (20) explained that the response of soil EC might be attributed more directly to variation in soil texture and their relationship improved in flooded conditions. When organic material decomposed, it mineralized H^+ which coupling with soil reduction process with increasing soil pH as well as mineralized cations to soil solution. The surface of decomposed organic material is naturally

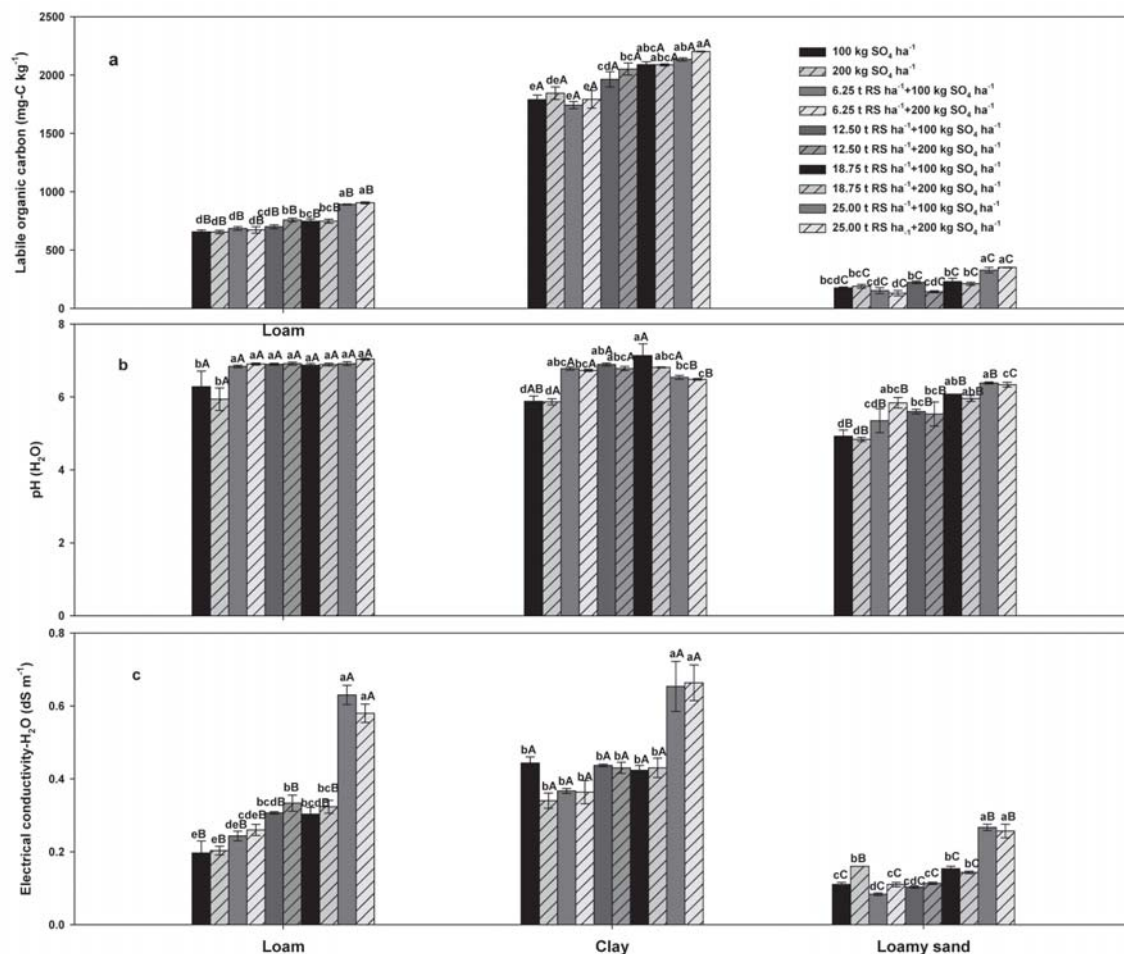


Fig 3 Labile organic carbon (a), pH (b) and electrical conductivity (c) in soil at different rates of rice straw and SO₄²⁻ application after 4 weeks of anoxic incubation. The lower case letters compare between the treatments within each soil type and the upper case letters compare the treatments between the three soil types, significantly different at $p \leq 0.05$ to 0.001. The vertical bars represented SE-mean

dominated by enormous amount of functional groups like carboxyl (R-COOH) and phenolic group ($\text{C}_6\text{H}_5\text{-OH}$). At the same time lactic, propionic, butyric, acetic and formic acids (source of carboxyl group) dissociate to release H⁺ (21) and the negative charges of those functional groups exposed on the decayed organic surface led to more ions (ionic concentration) in the soil system, rendering higher EC values. Simultaneously, these organic acids and LOC substrates are utilized by methanogens in methanogenesis. Furthermore, Han and He (22) reported that exogenous cellulase accelerated the decomposition of cellulose in

soil increasing soil EC with the straw incorporation. Hence, cellulose from rice straw decomposition is directly correlated to soil EC in this context.

4. Conclusions

Rice straw addition in incubated paddy soils significantly increased CH₄ production, but it gave other advantages to accelerate soil mechanisms which released ions, increasing EC, LOC, and pH by microbial decomposition. LOC contents and CH₄ productions were

determined by soil textures in this increasing order: clay > loam > loamy sand. SO_4^{2-} had potential for suppressing CH_4 production especially at the rate of 200 t/ha in clay and loamy sand soils. As rice straw and SO_4^{2-} are important sources of plant nutrients, further experiments should be established in the field trials for a more understanding of the increase of crop productivity due to rice straw and SO_4^{2-} application.

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